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ELECTRONIC AND IONIC TRANSPORT IN POLYMERS(U) TEXAS
UNIV AT ARLINGTON DEPT OF CHEMISTRY M POMERANTZ ET AL.
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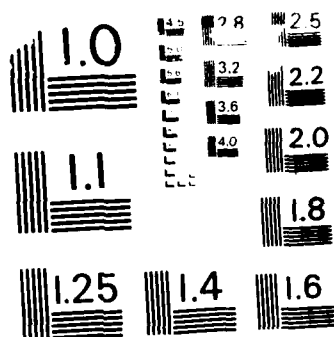
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<p>Ethylmercapto-substituted polythiophenes have been studied and the results have been compared to theoretically derived band structure and oligomer conformation. The quartz crystal microbalance has been shown to be an effective tool for studying ion exchange in doped conjugated polymers. Electrochemical studies of anion exchange in free standing polypyrrole tosylate membranes has been completed. The luminescence modulation of an interfacial probe during redox switching of polypyrrole has been shown to reflect the conductivity. PRDDO and ab initio spin density calculations have been correlated with the ability of a heteroaromatic monomer to be polymerized electrochemically. Similarly, conductivities have been correlated to both electronic structure and conformation of the polymer. Poly(azomethine) ethers have been prepared with a variety of (CH₂)_n spacer groups and these have been studied for their liquid crystalline properties.</p>					
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Technical Report

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Description of Progress

a) Electronically Conducting Polyheterocycles

A study of ethylmercapto-substituted polythiophenes has been completed including comparisons of theoretical modelling (below) of oligomer conformations and polymer band structure to experimental results. We have initiated experiments in the bulk electrolysis of substituted thiophenes at high surface area carbon felt electrodes in order to attain high yields of polythiophenes electrochemically.

The quartz crystal microbalance has been shown to be an effective tool for monitoring spontaneous ion exchange of various anions in doped complexes of conjugated polymers. The temperature dependence of the electrical conductivity of these complexes synthesized by ion exchange have been found to be independent of dopant ion identity, except for fluoride which degrades the polymer.

Studies on the anion exchange characteristics of self-standing polypyrrole membranes have been completed. Complementing the self-exchange behavior reported by the University of Massachusetts group for polypyrrole perchlorate are these new results for polypyrrole tosylate. The variables studied included bathing medium composition, its pH, and membrane morphology. Another significant result during this reporting period is the demonstration of fluorescence or luminescence modulation from an interfacial probe during redox switching of polypyrrole. Specifically, changes in the electronic conductivity of polypyrrole during redox switching is faithfully reflected in the intensity of luminescence from a probe molecule located within the critical energy-transfer quenching cross-section of the polypyrrole surface. To our knowledge, this is the first example of this type of an effect, which may have implications for chemical sensor applications. Finally, electrochemical characterization of substituted polythiophenes is in progress.

Extensive calculations at both the PRDDO and *ab initio* levels have been completed for a variety of substituted thiophenes. Spin density calculations have been successfully correlated with

the ability of a monomer to be polymerized electrochemically, and conductivities have been correlated to both the electronic structure and the conformation of the polymer. Methods for calculating band structures, including both the Extended Hückel and Valance Effective Hamiltonian methods, have now been implemented in our laboratory and are being used routinely for evaluating potential new conducting polymers. Calculations are now being extended to other polyheterocyclic systems.

Finally, Perturbation Molecular Orbital Theory (PMO), based on very simple odd alternate hydrocarbon fragments and Hückel M.O. theory, has been applied to a variety of conducting hydrocarbons. It provides band gaps, ionization potentials and electron affinities in reasonable agreement with reported measured values and with reported values calculated by much more sophisticated methodology. Since it is simple to apply and yet fairly reliable it should prove to be a useful tool for rapidly obtaining qualitative information on the electronic properties of such polymers.

b) Novel Liquid Crystalline Conductors

Two series of poly(azomethine) ethers have been prepared which contain n-alkyl spacer groups from pentyl to dodecyl in length. These polymers were prepared from either the bis(formylphenylene) ethers or bis(aminophenylene) ethers with the corresponding 1,4-diaminobenzene or terephthalaldehyde. Characterization of the liquid crystalline (LC) properties of these polymer systems will permit us to understand the importance of configurational isomerism within the mesogen. Specifically, these comparisons will involve the central terephthalidene structure relative to the bis(azomethinephenylene) structure, or simply the reversal of the nitrogen atom placement. Preliminary optical microscopy data indicates that the reversal of the N placement influences only thermal transition temperatures. In either series, only nematic mesomorphism has been observed. Full observation of the mesophase is not found until reaching a spacer length of eight or nine CH₂ units. Polymers with smaller spacer lengths decomposed within the nematic

phase. DSC experiments are in progress to collect more accurate transition temperature and thermodynamic data. In addition, synthesis of deuterated polymers is underway for ^2H NMR studies of the ordering in these systems.

Major Equipment

- 1) The Bruker ESP-300 Electron Spin Resonance Spectrometer is installed and running.
- 2) The Bruker MSL-300 solids-liquids multinuclear NMR Spectrometer has been delivered and is in the process of being set up. The Doty Scientific high speed CP/MAS probe has been delivered and samples can be routinely spun at 12-14 kHz.
- 3) A JEOL-1200EX Analytical Scanning Transmission Electron Microscope has been ordered. In addition to the \$100,000 from DARPA, the University has supplied \$137,000 in matching funds (\$237,000 total price) rather than the \$50,000 in matching funds originally in the budget.

Publications:

Papers Published

Jang, G-W; Tsai, E.W.; Rajeshwar, K. "Electrochemically-Triggered pH Modulation at the Ruthenium Oxide Electrolyte Interface: A Spectroelectrochemical Probe for the Proton Transport Mechanism," *J. Electrochem. Soc.* **134**, 2377 (1987).

Papers in Press

Panchalingam, V.; Reynolds J.R. "Structure of the Alternating Copolymer of 1,3-Cyclohexadiene and Chloroacrylonitrile," *Macromolecules*, in press.

Martinez, M.; Reynolds, J.R.; Basak, S.; Black, D.A.; Marynick, D.S.; Pomerantz, M. "Electrochemical Synthesis and Optical Analysis of Poly [(2,2'-dithienyl)-5,5'-divinylene]," *J. Polym Sci., Polym. Phys. Ed.*, in press.

Tsai, E.; Jang, G-W; Rajeshwar, K. "Proton Transport Accompanies Redox Switching of Polypyrrole: A Spectroelectrochemical Study," *J. Chem. Soc., Chem. Commun.*, in press.

Tsai, E.; Phan, L.; Rajeshwar, K. "Electrochemical Modulation of Luminescence from an Interfacial Probe during Redox Switching of Polypyrrole," *J. Phys. Chem.*, in press.

Shaffer, T.D. "Phase Transfer Catalyzed Polymerization of α,α' -Dibromoxylene Isomers," *J. Polym. Sci., Polym. Lett. Ed.*, in press.

Wang, S.J.; Naidu, S.V.; Sharma, S.C.; De, D.K.; Jeong, D.Y.; Black, T.D.; Krichene, S.; Reynolds, J.R.; Owens, J.M. "High T_c Superconductor $YBa_2Cu_3O_{7-\delta}$ Studied by Positron Annihilation," *Phys. Rev. B.*, in press.

Papers Submitted for Publication

Tsai, E.W., Pajkossy, T., Rajeshwar, K., and Reynolds, J.R. "Anion Exchange Behavior of Polypyrrole Membranes," *J. Phys. Chem.*, submitted for publication.

Reynolds, J.R., Sundaresan, N.S., Pomerantz, M., Basak, S., and Baker, C.K. "Self-Doped Conducting Copolymers: A Charge Transport Study of Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]}" *J. Electroanal. Chem.*, submitted for publication.

Meetings, Oral Presentations and Visitors

An invited paper entitled: "Chemical Diffusion in Polypyrrole," K. Rajeshwar, J. Reynolds, E. Tsai and T. Pajkossy, was presented at the Symposium on "Membrane Processes in Electrosynthesis" at the Fall National Meeting of the Electrochemical Society in Honolulu, Hawaii, in October.

A paper entitled: "A New Spectroelectrochemical Method for Measurement of pH Modulation at an Electrode/Electrolyte Interface" was presented by K. Rajeshwar at the Symposium on "Spectroelectrochemistry and Electroanalytical Science" at the Fall National Meeting of the Electrochemical Society in Honolulu, Hawaii, in October.

The following presentations were given by J.R. Reynolds:

San Jose State University, San Jose, CA, October 1987

"Polyheterocycles: Direct Control of the Electronic and Ionic Properties"

University of Dallas, Dallas, TX, November 1987

"Conductive Polymers: A Research Overview"

North Texas State University, Denton, TX, November 1987

"Conductive Polymers: A Research Overview"

J. R. Reynolds visited researchers at the IBM Research Laboratory in San Jose California, and discussed conductive polymers, quartz crystal microbalance applications and high temperature superconductors.

K. Rajeshwar presented a Departmental Colloquium entitled "Electrochemistry and Photoelectrochemistry of Conducting Oxides and Conducting Polymers," at UTA.

Visitors to the UTA Chemistry Department included Dr. E. Thomas Strom of the Mobil R and D labs in Dallas who spoke on Electron Spin Resonance Spectroscopy, Dr. Donald Woessner of the Mobil R and D labs in Dallas who spoke on Solid State NMR Spectroscopy, Prof. Howard Arnott of UTA who spoke on Electron Microscopy and Dr. Roger Goolsby of UTA who spoke on Mechanical Characterization of Materials.

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